Effective Date: 10/15/01

STL On-Site Technologies
STANDARD OPERATING PROCEDURE

TITLE : Volatile Organic Compounds (VOCs) by GC/MS

SUPERSEDES : (NONE)

Approvals and Signatures

Division Manager:	Peter A. Law	Date
QA Manager:	Robert S. DeGaetano	Date
Technical Director:	John V. Hawkins	Date

1.0 SCOPE AND APPLICATION

1.1 This SOP provides detailed procedures for determining volatile organic compounds in multi-media, multi-concentration samples.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, soil vapor, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils and sediments.

1.3 Compounds typically determined by this method and their MDL and PQL values are presented in Table 1 of this document.

1.4 It is the policy of STL and of the On-Site Technologies division to ensure that we administer contracts and orders for goods and services in a manner that is fully compliant with governmental laws and regulations, as well as the STL Policy Statement on Business Ethics and Conduct.

2.0 SUMMARY OF METHOD

2.1 Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2 Aqueous and air samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3 In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times.

3.0 DEFINITIONS

3.1 There are many definitions used within the laboratory that may be generic to all laboratory analyses or more specific for certain methods. For the most recent terms and definitions used within the laboratory, refer to the STL-OST Laboratory Quality Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3 Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5 Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5.0 SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all STL-OST associates.

5.2 The STL Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel should receive training in the CHP, including the written Hazard Communication plan, prior to working in the laboratory.

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.3.2 Chemicals known to be flammable are: Methanol.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of an STL-OST associate. The situation must be reported immediately to a laboratory supervisor.

6.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1 Holding times for all volatile analysis are 14 days from sample collection.

6.2 Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

6.3 Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

6.4 There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

6.5 Sample collection for medium level analysis using EnCore samplers.

6.5.1 Ship one 5 g (or 25 g) EnCore sampler per field sample position. An additional bottle must be shipped for percent moisture determination.

6.5.2 When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

6.5.3 Add the correct amount of surrogate spiking mixture.

6.5.4 Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples.

6.5.5 Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol.

6.5.6 Shake the samples for two minutes to distribute the methanol throughout the soil.

6.5.7 Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

6.6 Sample collection for medium level analysis using field methanol preservation

6.6.1 Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial VOA vial).

6.6.2 Seal the bottle and attach a label.

6.6.3 Weigh the bottle to the nearest 0.01g and note the weight on the label.

6.6.4 Ship with appropriate sampling instructions.

6.6.5 Each sample will require an additional bottle with no preservative for percent moisture determination.

6.6.6 At client request, the methanol addition and weighing may also be performed in the field.

6.6.7 When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

6.6.8 Add the correct amount of surrogate spiking mixture.

6.6.9 Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples.

6.6.10 Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol.

6.6.11 Shake the samples for two minutes to distribute the methanol throughout the soil.

6.6.12 Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

6.7 Low level procedure

6.7.1 If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

6.7.2 A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

6.7.3 The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

6.7.4 Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

6.7.5 Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

6.7.6 Weigh the vial to the nearest 0.1g and note the weight on the label.

6.7.7 Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

6.7.8 Note: Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at > -10°C until analysis.

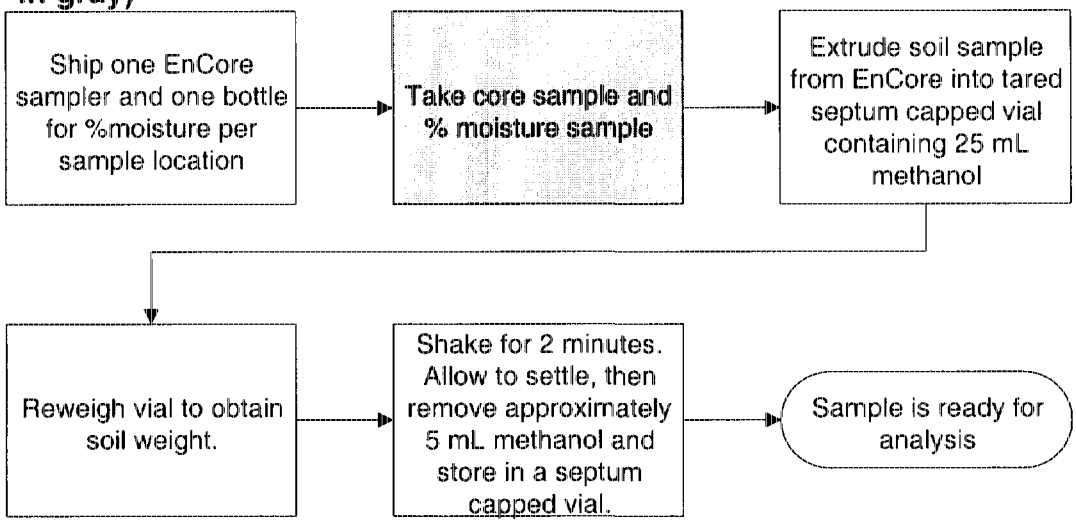
6.7.9 Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

6.8 Unpreserved soils

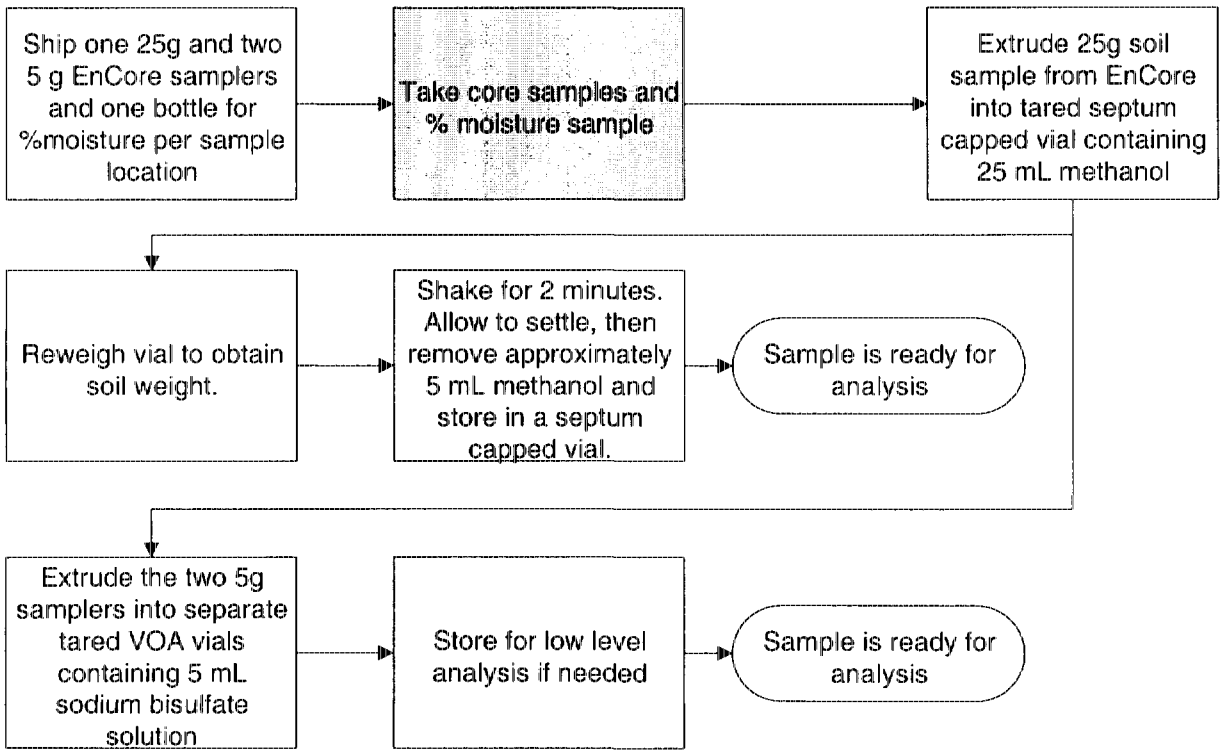
6.8.1 At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A where an aliquot of soil, typically 5 grams, is added directly to the sparge vessel containing 5 – 10 mls of water. Alternatively, the soil may be extracted in 5 mL of methanol and a 100uL aliquot of the extract added to 5 – 10 mL of water in the sparge vessel for medium/high level analysis.

6.8.2 The maximum holding time is 14 days from sampling until the sample is analyzed.

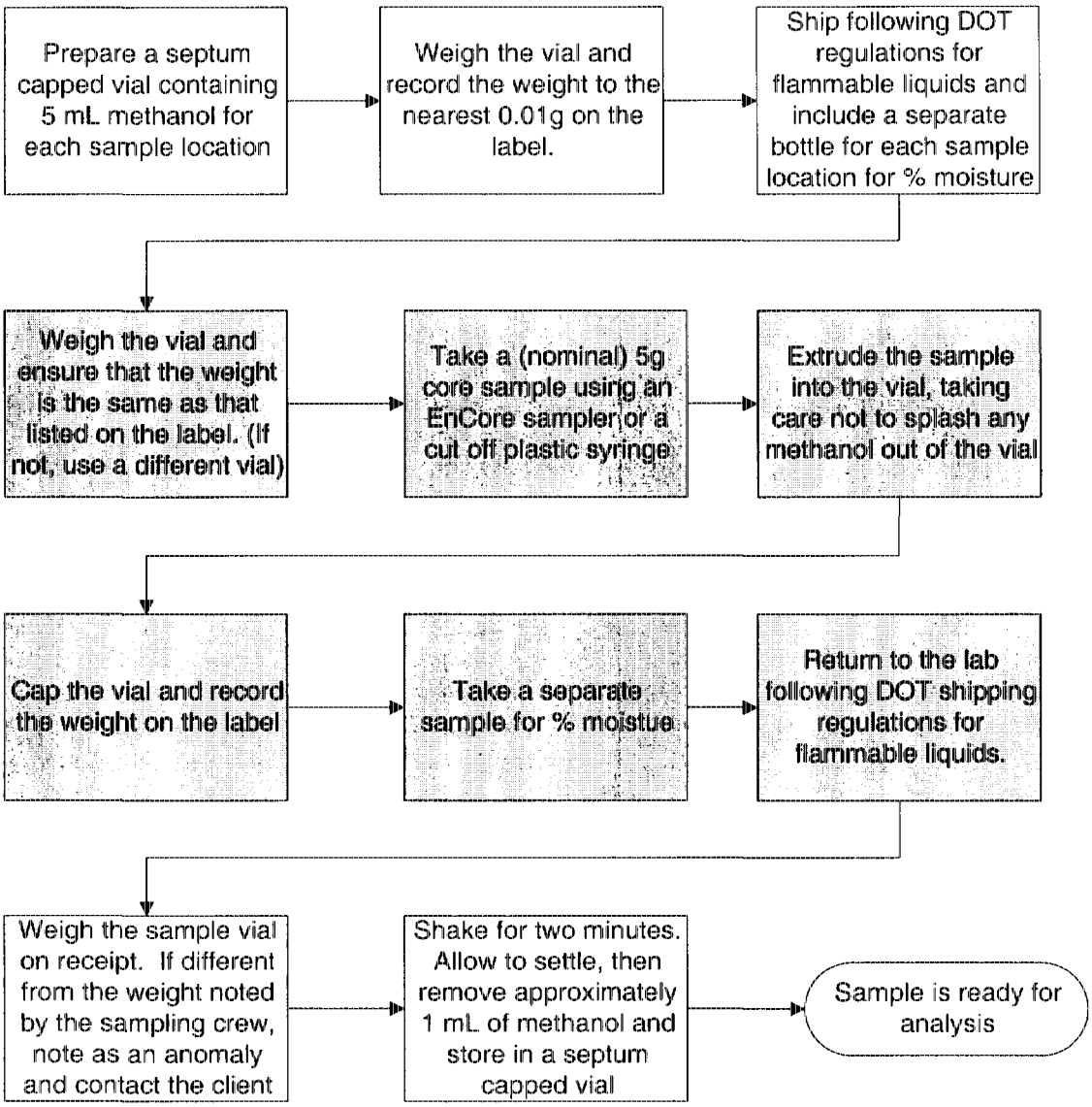
EnCore procedure when low level is not required (field steps in gray)



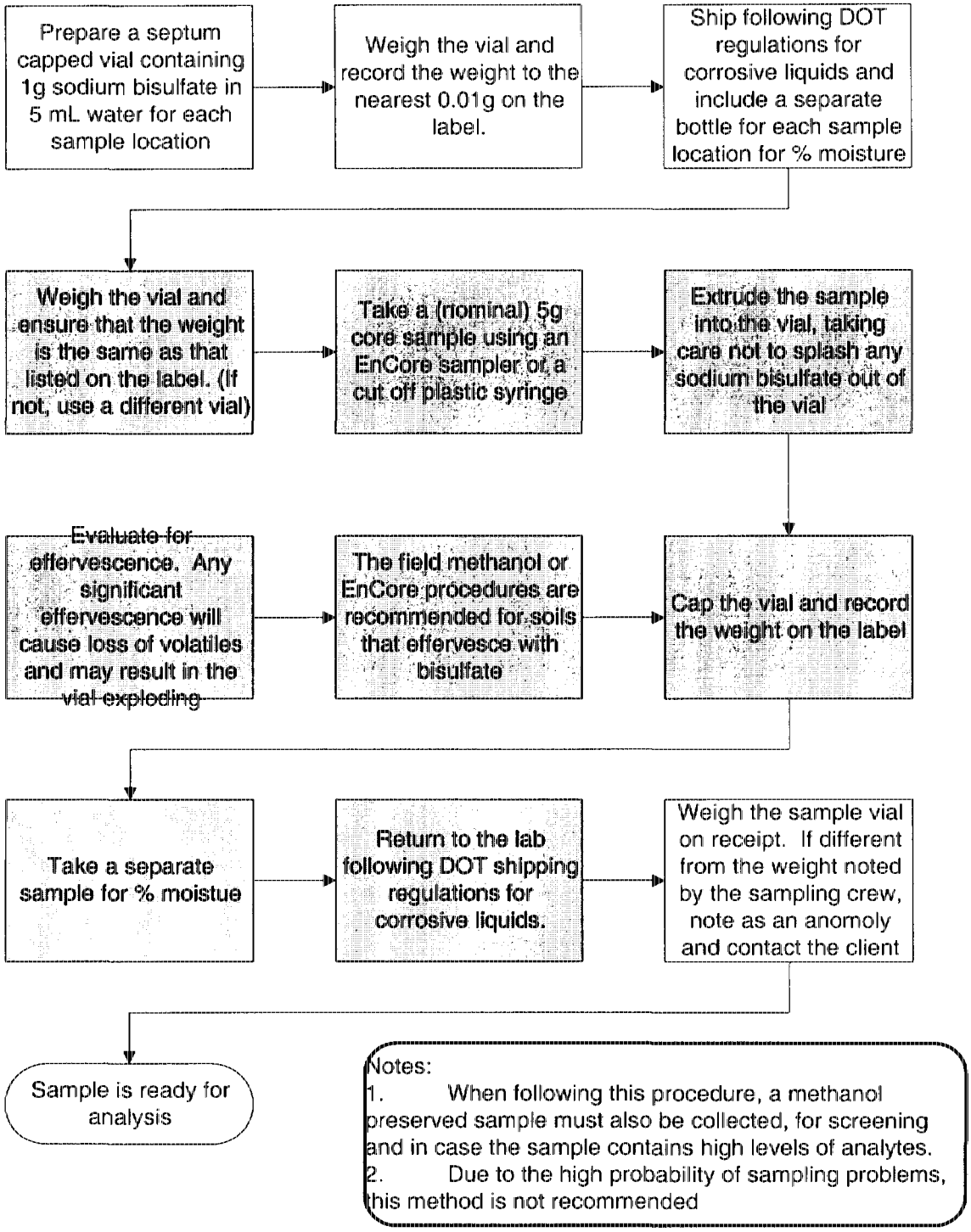
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



7.0 EQUIPMENT AND MATERIALS

7.1 Microsyringes: 10 uL and larger, 0.006 inch ID needle.

7.2 Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

7.3 Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

7.4 Glassware:

7.4.1 Vials: 20 mL with screw caps and Teflon liners.

7.4.2 Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

7.5 Spatula: Stainless steel.

7.6 Disposable pipets: Pasteur.

7.7 pH paper: Wide range.

7.8 Gases:

7.8.1 Helium: Ultra high purity, gr. 5, 99.999%.

7.8.2 Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

7.8.3 Compressed air: Used for instrument pneumatics.

7.9 Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

7.10 Gas Chromatograph/Mass Spectrometer System:

7.10.1 Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming. Most STL-OST laboratories utilize a Hewlett-Packard 5890 Series II gas chromatograph with 5972A Hewlett Packard Mass Selective Analyzer, or equivalent.

7.10.2 Chromatographic columns:

7.10.2.1 Column 1: DB-624 (J@W Scientific), 60 m x 0.32 mm ID

7.10.2.2 Column 2: VRX (J@W Scientific), 30m x 0.25mm ID

7.10.3 Sample concentrator:

7.10.3.1 OI Analytical model 4560 or model 4460A, or equivalent

7.10.4 Autosampler:

7.10.4.1 OI Analytical MPM-16 or DPM-16 Multiple Purging Modules (5030).

7.10.4.2 Varian Archon Purge and Trap Autosampler (5035).

7.10.5 Data acquisition system:

7.10.5.1 G1034C Operating Software and G1032C EnviroQuant Software, or equivalent, for data acquisition and reduction.

8.0 REAGENTS AND STANDARS

8.1 Methanol: Purge and Trap Grade, High Purity

8.2 Reagent Water: Purchased from Baxter or other equivalent vendor. Water is certified high purity, organic free, and is analyzed by STL-OST to show that it is free of interferences and therefore can be used for sample dilutions and as a lab blank.

8.3 Standards

8.3.1 Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10 to –20 °C.

8.3.2 Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer.

8.3.2.1 Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

8.3.3 Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

* Typically, stock calibration standard concentrations are 2000 ug/mL. However, the concentration may change based on availability of specific standards from approved vendors. From these stock solutions, an aliquot is taken and brought to volume in methanol to yield a final concentration of 25 ug/mL. Dilutions of the 25 ug/mL working standard are prepared in water at concentrations of corresponding to 5, 10, 20, 50 and 100 ug/L. Additional standard preparations may be required based on project specific data quality objectives. All preparation information is recorded in standard preparation logbooks.

8.3.4 Internal Standards: Internal standards are added to all samples, standards, and blank analyses. The internal standards utilized by this procedure are stated in method 8260B.

8.3.5 Surrogate Standards: Surrogate standards are added to all samples, standards, and blank analyses. The surrogates utilized by this procedure are stated in method 8260B.

* Typically, stock solutions of internal standard and surrogates are 2000 ug/mL. However, the concentration may change based on availability of specific standards from approved vendors. From these stock solutions, an aliquot is taken and brought to volume in methanol to yield a final concentration of 50 ug/mL. A total of 5 uL of the internal standard/surrogate working standard is added to 5 mL of sample to yield a final concentration of 50 ug/L.

8.3.6 Laboratory Control Sample (LCS) Spiking Solutions: Unless otherwise agreed upon as part of the project data quality objectives, the LCS spike mix will contain all target compounds for the particular investigation. The source of the LCS spiking solution is from a source other than the calibration standard, or from the same working standard as the calibration if an independent calibration verification sample from a different source was analyzed following initial calibration. The concentration levels and preparation procedures are identical to the calibration working standard with the final concentration at or near the midpoint of the initial calibration.

8.3.7 Matrix Spiking Solutions: Same as LCS

8.3.8 Tuning Standard: A standard made up that will deliver 50 ng on column upon injection. A working standard concentration of 25 ng/uL of 4-Bromofluorobenzene in methanol is recommended.

9.0 PROCEDURES

9.1 Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system. The use of separate calibrations is required for water and low soil matrices.

9.2 Recommended Instrument Conditions

General:

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250 °C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300□C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

Gas chromatograph suggested temperature program:

BFB Analysis

Isothermal:	170 °C

Sample Analysis

Initial Temperature:	40 °C
Initial Hold Time:	4 minutes
Temperature Program:	8 °C/minute
Final Temperature:	184 °C
Second Temperature	Program: 40 °C/minute
Final Temperature:	240 °C
Final Hold Time:	2.6 minutes

9.3 Instrument Tuning

9.3.1 Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 2 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

9.4 Initial Calibration

9.4.1 A series of five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Typical calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 ug/L. Certain analytes are prepared at higher concentrations due to poor purge performance.

9.4.2 Each calibration standard is analyzed and the response factors (RF) for each compound calculated using the area response of the characteristic ions against the concentration for each compound and internal standard.

9.4.2.1 The five system performance check compounds (SPCC) are checked for a minimum average response factor.

- System Performance Check Compounds (SPCC) average RF must be greater than or equal to 0.100 for chloromethane, 1,1-dichloroethane, and bromoform. SPCCs chlorobenzene and 1,1,2,2-tetrachloroethane average RF must be greater than or equal to 0.300.

9.4.2.2 The % RSD of the calibration check compounds (CCC) must be less than 30%.

- The CCC compounds are vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, and ethylbenzene.

9.4.2.3 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

9.4.2.4 The average RF must be calculated for each compound. If the %RSD is < 15%, then the average response factor for calibration may be used. Alternatively, if the average %RSDs for all compounds in the calibration is < 15%, then all analytes may use average response factor for calibration. However, any detected compounds with %RSD > 15% must be noted in the report, or a linear curve generated with the correlation coefficient, r, > 0.995 (coefficient of determination, r^2 for non-linear curves > 0.990).

9.5 Continuing Calibration: The initial calibration must be verified every twelve hours. Continuing calibration begins with analysis of BFB as described above.

9.5.1 If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3, or mid-level calibration standard is used for the continuing calibration.

9.5.2 The RF data are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds.

9.5.2.1 The % drift of the CCCs must be < 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described above.

9.5.2.2 If the CCCs and or the SPCCs do not meet criteria, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis.

9.6 Sample Analysis Procedures – Water Samples

9.6.1 Samples are removed from refrigerated storage and are signed out in the internal chain of custody form, or equivalent (if applicable). All samples are allowed to warm to room temperature.

9.6.2 Make sure all instrumental operating conditions are correctly set and BFB, calibration and blank criteria have been met.

9.6.3 In a gas tight 5-ml syringe, add 5-ml aliquot of sample that has been allowed to come to ambient temperature. Carefully pour the sample into the syringe barrel till just short of overflowing.

9.6.4 Replace the syringe plunger. After replacing the plunger, vent any residual air, then adjust the volume to 5.0 ml. Drop a few drops of the sample on narrow range pH paper (0-6pH range) and record the pH in the instrument logbook for all aqueous samples.

9.6.5 Next, add the internal standard and surrogate standards and load the syringe contents into the purge vessel (see SOP appendices for IS/SURR solution preparation and amount to add).

9.6.6 Water MS/MSD samples are prepared by spiking the sample aliquot with matrix spike standard in addition to internal standards and surrogate solutions (see SOP appendices for IS/SURR and MS/MSD/LCS solution preparation and amounts to add).

9.6.7 A method blank must be analyzed every 12 hours after the initial and/or continuing calibration criteria has been achieved. The method blank consists of 5 ml reagent water spiked with the internal standard and surrogate standards, and carried through the analytical procedure.

9.7 Sample Analysis Procedures – Low Level Soil Samples

9.7.1 Samples are removed from refrigerated storage and are signed out in the internal chain of custody form, or equivalent (if applicable). All samples are allowed to warm to room temperature.

9.7.2 Make sure all instrumental operating conditions are correctly set and BFB, calibration and blank criteria have been met.

9.7.3 Using a clean, dry culture tube, weigh out 5 grams of sample and add the internal standard and surrogate standards.

9.7.4 Add 5-ml reagent water to the culture tube in the same manner as a water sample. The sample is now ready for heated purge and analysis.

9.7.4.1 Low-level soil samples are analyzed using the same calibration curve as water samples (assuming the calibration curve was analyzed using a heated-purge).

9.8 Sample Analysis Procedures – Medium Level Soil Samples

9.8.1 If high levels of volatiles are expected, then the samples collected should be field preserved in methanol.

9.8.2 Alternatively, the client may request the EnCore sampler or equivalent. Therefore, the plug of soil from the EnCore sampler is placed into the pre-weighed VOA jar containing 10-mls of purge and trap grade methanol. Record the weight of the jar, soil and methanol. Record the soil weight on the jar. Swirl to mix the contents, then let the contents settle and transfer 1-2mls of the methanol extract into an extract vial. Store extract until time of analysis. It is also possible that a low-level soil is actually a high level soil. Therefore the methanol extraction is performed at the laboratory.

9.8.3 If the sample is extracted at the laboratory, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula.

9.8.4 A medium level soil extract is prepared by weighing out 5.0 grams of sample into a 20-ml extraction vial, record the weight to the nearest 0.1-gram. Determine the percent moisture (see SOP # OSS00803.MA).

9.8.5 Quickly add 5.0 ml of purge and trap grade methanol to the vial. Swirl the vial to mix contents and allow the soil to settle.

9.8.6 Using a disposable pipette, transfer about 1 ml of sample extract to a GC vial for storage. The remainder of the extract may be discarded. Transfer about 1 ml of the reagent methanol to a labeled GC vial for use as the method blank. These extracts may be stored in the dark at 4 ± 2 °C prior to analysis.

9.8.7 In a gas-tight 5-ml syringe, add 5 ml of reagent water and fortify it with the IS/Surrogate spiking solution using a 10 µl gas-tight syringe, and 100 µl of sample extract using a 250 µl gas tight syringe. Transfer the sample to the purge vessel on the autosampler.

9.8.8 If an extract is analyzed which contains target compounds at concentrations greater than the initial calibration upper limit, then the extract must be reanalyzed at an appropriate dilution. Volumes of less than 10 µl (i.e. 10 fold MLS dilution) shall be prepared diluting an aliquot of the methanol extract and then taking 100 µl for analysis. Add the volume of methanol extract from the sample and a volume of clean methanol to total 100 µl. The total methanol volume added shall be 100 µl, excluding the methanol in the standards.

9.9 Qualitative Analysis – Target Compounds

9.9.1 The relative retention time of a target compound must be within +/- 0.06 RRT units of the RRT of the calibration standard for a positive identification. For reference the standard must be analyzed within the same 12 hour time period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT shall be assigned by using the extracted ion current profiles for ions unique to the component of interest.

9.9.2 In addition, a comparison must be made between the mass spectrum obtained in the sample analysis and the reference mass spectrum for that compound, which was obtained on that specific GC/MS system. The requirements for qualitative verification by comparison of mass spectra are as follows:

9.9.2.1 All ions present in the reference spectrum at an intensity greater than 10% must be present in the sample spectrum.

9.9.2.2 The relative intensities of the ions above 10% must agree with 20% between the reference and sample spectra.

9.9.2.3 Ions greater than 10% in the sample spectrum but not present in the reference spectrum must be considered and accounted for by the analyst.

9.9.2.4 If a compound cannot be verified by the above criteria, but in the technical judgment of the analyst, the identification is correct, then the compound shall be reported.

9.10 Tentatively Identified Compounds

9.10.1 If requested a library search shall be performed for non-target compounds in the sample for purposes of tentative identification. For this purpose, the most recent release of the NIST mass spectral library shall be used.

9.10.2 Up to 10 organic compounds of apparent concentration not listed in Table 1.0, shall be tentatively identified via a forward library search. Only compounds with responses greater than 10% of the closest IS exhibiting no interference are to be searched.

9.10.3 The ChemStation software is utilized to perform the automated library search. The program (TICS) is executed with the data file, quantitation file, and number of compounds to be searched, specified for each sample or blank. Prior to running the program, the analyst must delete from the quantitation file, using the QDEL program, the non-TCL compounds identified in the quantitation file. This will facilitate the automated search using the program. If the non-TCL positive hits are not removed prior to executing the program, they would be counted as target compounds and not be searched by the program, leading to false negatives.

9.10.4 A tentative identification will be made after a comparison between the mass spectrum obtained in the sample analysis and the library search mass spectra found for that compound. The requirements for tentative verification by comparison of mass spectra are as follows:

9.10.4.1 Ions present in the reference spectrum at an intensity greater than 10% should be present in the sample spectrum.

9.10.4.2 The relative intensities of the ions above 10% should agree with 20% between the reference and sample spectra.

9.10.5 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or coeluting compounds.

9.10.6 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible background subtraction by the data system.

9.10.7 If in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound shall be reported as unknown. Additional classification shall be made if possible (i.e. Unknown hydrocarbon).

10.0 QUALITY CONTROL

10.1 Initial Demonstration of Capability

10.1.1 For the standard analyte list, the initial demonstration of capability (IDOC) and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples.

10.1.2 For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

10.2 Control Limits

10.2.1 Historical control limits are determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually.

10.2.1.1 For new projects and/or sites without historical data, default limits of 70 – 130% for the LCS and MS recoveries will be used until enough data points are collected.

10.2.1.2 Alternatively, control limits may be determined and agreed upon with the client based on the data quality objectives of the project.

10.3 Surrogates

10.3.1 Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits.

10.3.2 If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

10.3.2.1 Check all calculations for error.

10.3.2.2 Ensure that instrument performance is acceptable.

10.3.2.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

10.3.2.4 Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. The decision to reanalyze or flag the data should be made in consultation with the client. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary.

10.4 Method Blanks

10.4.1 For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples.

10.4.1.1 For low-level volatiles, the method blank consists of reagent water.

10.4.1.2 For medium-level volatiles, the method blank consists of methanol.

10.4.2 Surrogates are added and the method blank is carried through the entire analytical procedure.

10.4.3 The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below), or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

10.4.3.1 If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

10.4.3.2 Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

10.4.3.3 If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

10.4.4 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

10.4.5 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

10.5 Laboratory Control Samples (LCS)

10.5.1 For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest and must contain the same analytes as the matrix spike. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

10.5.1.1 If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS.)

10.5.1.2 If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

10.6 Matrix Spikes

10.6.1 For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 3. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

10.6.1.1 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

10.6.1.2 If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

10.6.1.3 If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

10.6.1.4 The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

10.7 Nonconformance and Corrective Action

10.7.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

11.0 CALCULATIONS

11.1 Response factor (RF):

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:
A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the specific internal standard
C_{is} = Concentration of the specific internal standard, ng
C_x = Concentration of the compound being measured, ng

11.2 Standard deviation (SD):

Equation 2

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N - 1}}$$

X_i = Value of X at i through N
N = Number of points
X = Average value of X_i

11.3 Percent relative standard deviation (%RSD):

Equation 3

$$\%\,RSD = \frac{\textbf{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = **Mean of RF values in the curve**

11.4 Percent drift between the initial calibration and the continuing calibration:

Equation 4

$$\%\ \textbf{Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where
$C_{expected}$ = Known concentration in standard
C_{found} = Measured concentration using selected quantitation method

11.5 Quantitative Analysis – Target Compounds

11.5.1 The relative response factor (RRF) from the initial calibration standard or the equation for linear regression is used to calculate the concentration in the sample depending on the percent RSD in the calibration curve.

11.5.2 Water Samples

Equation 5

$$\mu g/L = \frac{(Ax)(Is)(Df)}{(Ais)(RRF)(Vo)}$$

where,

Ax	=	area of the compound quantitation ion
Ais	=	area of IS quantitation ion
Is	=	IS amount in nanograms
RRF	=	Average Relative Response Factor from the Initial calibration curve
Vo	=	volume of water purged in ml's
Df =		Dilution factor.

11.5.3 Medium Level Soil Samples (dry weight basis)

Equation 6

$$\mu g/Kg = \frac{(Ax)(Is)(Vt)(1000)(Df)}{(Ais)(RRF)(Va)(Ws)(D)}$$

where,
Ax, Is, Ais and RRF are as given for water.

$$D = \frac{100 - \%\ moisture}{100}$$

RRF = Average Relative response factor from the ambient temperature purge of the initial calibration curve.

Ws =	weight of sample extracted in grams
Vt =	total volume of methanol extract in ml
Va =	volume of the methanol extract added in μl
Df =	Dilution factor. For medium level soils, the number of microliters (μl) of methanol added to the reagent water for purging (i.e. Va above) to the number of μl of the methanol extract of the sample contained in that volume Va. The dilution factor is equal to one in all cases other than those requiring dilution of the methanol extract.

11.6 MS/MSD Recovery

Equation 7

$$\textbf{Matrix Spike Recovery, } \% = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result

SR = Sample result

SA = Spike added

11.7 Relative % Difference calculation for the MS/MSD

Equation 8

$$\mathbf{RPD} = \frac{|\mathbf{MSR - MSDR}|}{\frac{1}{2}(\mathbf{MSR + MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

11.8 Tentatively Identified Compounds

11.8.1 An estimated concentration for non-target compounds tentatively identified in the sample shall be determined by the internal standard method. For quantitation, the nearest IS free of interferences shall be used.

11.8.2 The equation used for calculating compound concentration is the same as above. Total area counts from the total ion chromatograms are used for both the IS and compound. A RRF of 1.0 is assumed and the resulting concentration shall be qualified as "J" (estimated), indicating the quantitative and qualitative uncertainties associated with this non-target compound.

11.8.3 meta and para Xylene isomers are to be reported as m&p-Xylene (total). The meta and para isomers coelute on the capillary column, therefore, special attention must be given to their quantitation. The area from the o-Xylene is quantitated separately. All three isomers must be present in the initial and continuing calibration standards.

11.8.4 If the on-column concentration of any compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and purged. Guidance in performing dilutions, and exceptions to this requirement are as follows:

11.8.4.1 Use the results of the original analysis to determine the approximate dilution factor required for the largest analyte peak within the initial calibration range.

11.8.4.2 The dilution factor chosen shall keep the response of the largest analyte in the upper half of the calibration range of the instrument.

12.0 DATA REDUCTION and REVIEW

12.1 Hardcopies of all instrument calibration, calibration verification and daily analytical sequence raw data shall be assembled into "packages" for review.

12.1.1 A thorough review of all chromatograms and associated ion profiles is performed by qualified analysts to ensure retention times are correct and relative abundances match library and/or reference spectra.

12.2 Analysts are responsible for reviewing the packages to evaluate the accuracy of transcriptions, the instrument's performance, and the calculated results. Section 10 details the acceptance criteria and corrective actions for instrument/batch QA/QC.

12.3 All necessary documentation to support corrective actions performed shall be included with the packages and available for review.

12.4 Preliminary results may be reported to the client at this time.

13.0 REPORTING OF RESULTS

13.1 Prior to generating a final report of results, the data is reviewed a second time. In addition to the method review performed by the first chemist, the second review includes a verification of any project/client specific criteria and a sensibility check.

13.2 If for any reason there is a question regarding the technical soundness of the data, it is brought directly to the attention of the Technical Director and/or Quality Assurance Manager.

13.3 After completing the secondary review, the final results are reported to the client in hardcopy form and/or electronic deliverable, if requested.

14.0 POLLUTION PREVENTION

14.1 Where possible, all STL-OST methods utilize very small quantities of extraction solvents to minimize pollution.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 Solvent waste must be disposed of in clearly labeled waste cans.

15.2 Acid waste must be collected in clearly labeled acid waste containers.

15.3 Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4 Refer to the Laboratory Sample and Waste Disposal plan.

15.5 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16.0 SUPPLEMENTAL DOCUMENTS – N/A

17.0 REFERENCES

17.1 "Test Methods for Evaluating Solid Waste", USEPA-SW846, Third Edition, September 1986 with all current revisions, method 8260B.

18.0 SUBSTANTIVE REVISIONS

18.1 Original issue – 05/11/01

18.2 Revision – 10/15/01

TABLE 1.0
TARGET COMPOUNDS AND REPORTING LEVELS

Compound	Report Limit (ug/L)	Report Limit (ug/kg)
1,1,1,2-Tetrachloroethane	5	500
1,1,1-Trichloroethane	5	500
1,1,2,2-Tetrachloroethane	5	500
1,1,2-Trichloroethane	5	500
1,1,-Dichloropropene	5	500
1,1-Dichloroethane	5	500
1,1-Dichloroethene	5	500
1,2,3-Trichlorobenzene	5	500
1,2,3-Trichloropropane	5	500
1,2,4-Trichlorobenzene	5	500
1,2,4-Trimethylbenzene	5	500
1,2-Dibromo-3-chloropropane	5	500
1,2-Dibromoethane	5	500
1,2-Dichlorobenzene	5	500
1,2-Dichloroethane	5	500
1,2-Dichloropropane	5	500
1,3,5-Trimethylbenzene	5	500
1,3-Dichlorobenzene	5	500
1,3-Dichloropropane	5	500
1,4-Dichlorobenzene	5	500
2,2-Dichloropropane	5	500
2-Butanone	10	1000
2-Chloroethylvinylether	5	500
2-Chlorotoluene	5	500
4-Chlorotoluene	5	500
4-isopropyltoluene	5	500
Acetone	10	1000
Benzene	5	500
Bromobenzene	5	500
Bromochloromethane	5	500
Bromodichloromethane	5	500
Bromoform	5	500
Bromomethane	10	1000
Carbon Disulfide	5	500
Carbon tetrachloride	5	500
Chlorobenzene	5	500
Chloroethane	10	1000
Chloroform	5	500
Chloromethane	10	1000
cis-1,2-Dichloroethene	5	500
cis-1,3-Dichloropropene	5	500
Dibromochloromethane	5	500
Dibromomethane	5	500
Dichlorodifluoromethane	5	500
Ethylbenzene	5	500
Hexachlorobutadiene	5	500
Isopropylbenzene	5	500
m&p-Xylenes	5	500
Methyl t-butyl ether	5	500
Methylene chloride	5	500
Naphthalene	5	500
n-Butylbenzene	5	500
n-Propylbenzene	5	500
O-Xylene	5	500
sec-Butylbenzene	5	500
Styrene	5	500
tert-Butylbenzene	5	500
Tetrachloroethene	5	500
Toluene	5	500
trans,1,2-Dichloroethene	5	500
trans-1,3-Dichloropropene	5	500
Trichloroethene	5	500
Trichlorofluoromethane	5	500
Vinyl chloride	10	1000

TABLE 2.0
GC/MS INSTRUMENT PERFORMANCE CRITERIA
4-BROMOFLUOROBENZENE (BFB)

m/z	Ion Abundance Criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	Less than 2 percent of mass 174
174	Greater than 50% of mass 95
175	5-9% of mass 174
176	95-101% of mass 174
177	5-9% of mass 176

TABLE 3.0
MATRIX SPIKE RECOVERY AND RELATIVE PERCENT DIFFERENCE LIMITS

Compound	% Recovery Water	RPD Water	% Recovery Soil	RPD Soil
1,1-Dichloroethane	61-145	14	59-172	22
Trichloroethene	71-120	14	62-137	24
Benzene	76-127	11	66-142	21
Toluene	76-125	13	59-139	21
Chlorobenzene	75-130	13	60-133	21

TABLE 4.0
SYSTEM MONITORING COMPOUND RECOVERY LIMITS

Compound	% Recovery Water	% Recovery Soil
Dibromofluoromethane	86 – 118	80 – 120
1,2-Dichloroethane-d_4	80 – 120	80 – 120
Toluene-d_8	88 - 110	81 - 117
Bromofluorobenzene	86 - 115	74 - 121

TABLE 5.0
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING TARGET COMPOUNDS AND SYSTEM MONITORING COMPOUNDS ASSIGNED FOR QUANTITATION

Fluorobenzene	**Chlorobenzene-d_5**	**1,4-Dichlorobenzene-d_4**
Chloromethane	Dibromochloromethane	1,1,2,2-Tetrachloroethane
Bromomethane	Chlorobenzene	1,2,3-Trichloropropane
Vinyl Chloride	1,1,1,2-Tetrachloroethane	n-Propylbenzene
Chloroethane	Ethylbenzene	2-Chlorotoluene
Dichlorofluoromethane	m&p-Xylene	4-Chlorotoluene
Trichlorofluoromethane	o-Xylene	1,3,5-Trimethylbenzene
Methylene Chloride	Styrene	tert-Butylbenzene
1,1-Dichloroethene	Bromoform	1,2,4-Trimethylbenzene
1,2-Dichloroethene (cis, trans)	Isopropylbenzene	sec-Butylbenzene
1,1-Dichloroethane	Bromobenzene	1,3-Dichlorobenzene
Methyl tert-butyl ether	Toluene-d_8 (smc)	4-Isopropyltoluene
Bromochloromethane	4-Bromofluorobenzene (smc)	1,4-Dichlorobenzene
Chloroform		1,2-Dichlorobenzene
1,1,1-Trichloroethane		n-Butylbenzene
Carbon tetrachloride		1,2-Dibromo-3-chloropropane
Benzene		1,2,4-Trichlorobenzene
1,2-Dichloroethane		Hexachlorobutadiene
Trichloroethene		Naphthalene
1,2-Dichloropropane		1,2,3-Trichlorobenzene
Bromodichloromethane		
1,3-Dichloropropene (cis, trans)		
Toluene		
2-Chloroethylvinylether		
Tetrachloroethene		
Dibromofluoromethane (smc)		
1,2-Dichloroethane-d_4 (smc)		

TABLE 6.0
CHARACTERISTIC IONS FOR SYSTEM MONITORING COMPOUNDS AND INTERNAL STANDARDS FOR VOLATILE ORGANIC COMPOUNDS

System Monitoring Compounds	Primary Ion	Secondary Ion(s)
Dibromofluoromethane	113	111
1,2-Dichloroethane-d_4	65	67
Toluene-d_8	98	100
4-Bromofluorobenzene	95	174, 176

Internal Standards	Primary Ion	Secondary Ion(s)
Fluorobenzene	96	77
Chlorobenzene-d_5	117	119
1,4-Dichlorobenzene-d_4	152	151

TABLE 7.0 - CHARACTERISTIC IONS FOR VOLATILE TARGET COMPOUNDS

Analyte	Primary Ion*	Secondary Ion(s)
Chloromethane	50	52
Bromomethane	94	96
Vinyl Chloride	62	64
Chloroethane	64	66
Methylene Chloride	84	49, 51, 86
Acetone	43	58
Carbon Disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	43**	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon Tetrachloride	117	119, 121
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	----
cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254, 256
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	91	92
Chlorobenzene	112	114
Ethylbenzene	106	91
Styrene	104	78, 103
Total Xylenes	106	91